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(54) METHOD FOR FORMING HYDROPHOBIC POROUS SOG FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for forming a hydrophoblic porous SOG film that is an interlayer insulation film having a low relative permittivity and prevents water from coming into from the surface of the SOG film, to reduce moisture absorbency, where the relative permittivity does not change even if another interlayer insulation film is laminated on the SOG film by a CVD process or the like after forming the interlayer insulation film.
SOLUTION: An organic silane solution containing silane, water, and alcohol is used, and the organic silane is subjected to acid or alkali hydrolytic treatment and thermally treated in the presence of a surface active agent, through which a porous SiO_2 film is obtained. Then, any of SiO_2 film, SiN_x film, and SiO_xN_y film is formed on the surface of the porous SiO_2 film by the CVD method or sputtering, to cap the surface.

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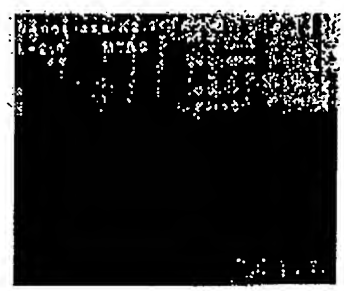

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JAPANESE [JP,2002-252225,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART TECHNICAL PROBLEM MEANS
EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The production approach of the hydrophobing porosity SOG film characterized by giving this organic silane to acidolysis or alkali hydrolysis, obtaining porosity SiO2 film by heat-treating under existence of a surfactant, forming either SiO2 film, the SiNx film or the SiOxNy film in the front face of the porous membrane subsequently obtained by the CVD method or the spatter using the organic silane liquid containing an organic silane, water, and alcohol, and capping this front face.
[Claim 2] The production approach of the hydrophobing porosity SOG film according to claim 1 characterized by being the organic oxy-silane which can hydrolyze said organic silane, and a surfactant being a cationic surfactant.
[Claim 3] Said organic silane is TEOS or TMOS. A surface active agent Lauryl trimethylammonium chloride, n-hexadecyl trimethylammonium chloride, an alkyl trimethylammonium star's picture, Cetyl trimethylammonium chloride, a cetyl trimethylammonium star's picture, Stearyl trimethylammonium chloride, alkyldimethyl ethyl ammonium chloride, An alkyldimethyl ethylammonium star's picture, cetyldimethylethyl ammonium bromide, An octadecyl dimethyl ethylammonium star's picture, Or the production approach of the hydrophobing porosity SOG film according to claim 1 or 2 characterized by being the alkyl halide trimethylammonium system cationic surfactant chosen from methyl dodecylbenzyl trimethylammonium chloride etc.
[Claim 4] The production approach of the hydrophobing porosity SOG film according to claim 1 to 3 characterized by using the acid for 8-15 mols of water, acidolysis, or alkali hydrolysis, 0.5-1.5 mols of alkali, and 0.1-0.4 mols of surfactants to one mol of said organic silanes.
[Claim 5] Mix an organic silane, water, alcohol, and an acid or alkali, and on a semi-conductor substrate, carry out the spin coat of the organic silane liquid which added the surfactant further, and it is heat-treated. Porosity SiO2 film is obtained by making this water, alcohol, and a surfactant evaporate. Subsequently The production approach of the hydrophobing porosity SOG film characterized by forming either SiO2 film, the SiNx film or the SiOxNy film in the front face of the obtained porous membrane, and capping this front face by the CVD method or the spatter.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the production approach of the porosity SOG film, especially the production approach of the hydrophobing porosity SOG film.
[0002]
[Description of the Prior Art] While copper (Cu) wiring is introduced in the field of LSI in recent years, the researches and developments about wiring structure, an interlayer insulation film, etc. are done. Since it is difficult to decrease wiring delay effectively only by using Cu wiring, making this oxide film into porosity is proposed from a viewpoint of obtaining the film with still lower specific inductive capacity in a semi-conductor process, using the low specific-inductive-capacity oxide film (SiO2 film) as an interlayer insulation film. For example, forming porosity SiO2 film of low specific inductive capacity by silanizing inorganic [SOG] is proposed using the method of applying the conventional SOG (spin on glass). Moreover, plasma CVD is used, a plasma polymerization is carried out using an organic silane, and forming SiO2 film of low specific inductive capacity is also proposed.
[0003]
[Problem(s) to be Solved by the Invention] When the laminating of the film is further carried out on it in semi-conductor processes, such as a CVD process, after formation of SiO2 film by the conventional approach, there is a problem that specific inductive capacity will rise. In the case of porosity SiO2 film formed using inorganic [SOG], in the case of that it is difficult for the path of a hole to become large too much, to form detailed pore, and to make specific inductive capacity a low value, and SiO2 film formed using the organic silane, there are also not enough problems that heat-resistant temperature is low (450 degrees C or less), in respect of membraneous quality.
[0004] Then, this invention persons did patent application as an application for patent No. 101478 [2000 to] as of April 3, Heisei 12 about the production approach of the porosity SOG film that are the interlayer insulation film of low specific inductive capacity, and specific inductive capacity does not change even if it carries out the laminating of the film further on it according to the CVD process after this interlayer insulation film formation etc., in order to cancel the fault of the above-mentioned conventional technique. However, by porosity SiO2 film obtained in this case, since that hole is carrying out orientation perpendicularly to the substrate, invasion of the moisture of the steam from a film front face etc. may become a problem. Moreover, since the inorganic SOG film contains a lot of OH radicals and an unreacted OH radical may remain also after baking, the moisture in an ambient atmosphere sticks to this residual OH radical, and there is also a problem of corroding wiring of aluminum etc.
[0005] This invention is the interlayer insulation film of low specific inductive capacity which prevented invasion of the moisture from a film front face, and suppressed moisture absorption, and even if it carries out the laminating of the film further on it according to the CVD process after this interlayer insulation film formation etc., it makes it a technical problem to offer the production approach of the hydrophobing porosity SOG film that specific inductive capacity does not change, while canceling the fault of the above-mentioned conventional technique.
[0006]
[Means for Solving the Problem] this invention persons have developed wholeheartedly so that they may suppress moisture absorption of the obtained film, while they develop wholeheartedly so that they may choose various ingredients and may find out a suitable ingredient and a suitable reaction condition in order to obtain porosity SiO2 film of low specific inductive capacity from a viewpoint that the specific inductive capacity of an interlayer insulation film is so desirable that it is low, with a spin coat method. Consequently, by obtaining porosity SiO2 film, and subsequently capping namely, covering the front face of this porous membrane with the film which consists of a specific ingredient by adding a surfactant to the system of reaction using an organic silane, even if specific inductive capacity is low and forms a cascade screen in the semi-conductor process after film formation, it succeeds in obtaining porosity SiO2 film which does not have change in specific inductive capacity and by which hydrophobing was carried

out, and it came to complete this invention.
[0007] Using the organic silane liquid containing an organic silane, water, and alcohol, the production approach of the hydrophobing porosity SOG film of this invention gives this organic silane to acidolysis or alkali hydrolysis, obtains porosity SiO2 film by heat-treating under existence of a surfactant, forms either SiO2 film, the SiNx film or the SiOxNy film in the front face of the porous membrane subsequently obtained by the CVD method or the spatter, and consists of capping this front face. Thereby, while moisture absorption of porous membrane is suppressed, even if it forms a cascade screen in the semi-conductor process of a back process, hydrophobing porosity SiO2 film which does not have change in specific inductive capacity can be obtained.
[0008] An organic silane is an organic oxy-silane of TEOS (tetramethyl orthochromatic silicate) or TMOS (tetramethoxy silane) which can be hydrolyzed. A surfactant A cationic surfactant, especially lauryl trimethylammonium chloride, n-hexadecyl trimethylammonium chloride, an alkyl trimethylammonium star's picture, Cetyl trimethylammonium chloride, a cetyl trimethylammonium star's picture, Stearyl trimethylammonium chloride, alkyldimethyl ethyl ammonium chloride, An alkyldimethyl ethylammonium star's picture, cetyldimethylethyl ammonium bromide, It is desirable that it is the alkyl halide trimethylammonium system cationic surfactant chosen from an octadecyl dimethyl ethylammonium star's picture or methyl dodecylbenzyl trimethylammonium chloride.
[0009] As for the amount of each raw material used, it is desirable to use the acid for 8-15 mols of water, acidolysis, or alkali hydrolysis, 0.5-1.5 mols of alkali, and 0.1-0.4 mols of surfactants to one mol of organic silanes. If the specific inductive capacity of the film obtained as water is less than eight mols does not become small but exceeds 15 mols, the solid-state of SiO2 deposits. A predetermined reaction does not advance with an acid and alkali being less than 0.5 mols, but if it exceeds 1.5 mols, the system of reaction will solidify. The specific inductive capacity of the film obtained as a surfactant is less than 0.1 mols becomes high, and if it exceeds 0.4 mols, membraneous quality will worsen. In addition, it is added in order to adjust the concentration of the whole reaction mixture, and according to the viscosity of reaction mixture, the amount is adjusted and alcohol is added so that it may be easy to apply.
[0010] Moreover, the production approach of the hydrophobing porosity SOG film of this invention Mix an organic silane, water, alcohol, and an acid or alkali, and on a semi-conductor substrate, carry out the spin coat of the organic silane liquid which added the surfactant further, and it is heat-treated. Porosity SiO2 film as an interlayer insulation film is obtained by making this water, alcohol, and a surfactant evaporate. Subsequently It consists of forming either SiO2 film, the SiNx film or the SiOxNy film in the front face of the obtained porous membrane, and capping this front face by the CVD method or the spatter.
[0011]
[Embodiment of the Invention] The production approach of hydrophobing porosity SiO2 film of this invention As described above, the organic silane liquid containing an organic silane, water, and alcohol is used. Apply what added the surfactant in the liquid obtained by ****** which gives this to acidolysis or alkali hydrolysis on a semi-conductor substrate, and it is heated under existence of a surfactant. Porosity SiO2 film is obtained by removing the matter, evaporating water, alcohol, and a surfactant, when other organic substances etc. are contained in the system of reaction and. Subsequently By the CVD method or the spatter, the hydrophobic film is formed in the front face of the obtained porous membrane, and this front face is capped. It becomes possible by many opening parts' (voidage's: about 60%'s or more) arising in the film, and becoming porosity in this way, and capping this porous membrane by the specific film to suppress invasion of moisture as a surfactant evaporates.
[0012] If it is the organic oxy-silane which was described above and which can be decomposed as a raw material silane, it will be used without being restricted especially. As alcohol, if it is alcoholic system solvents, such as ethyl alcohol and isopropyl alcohol, it will be used, without being restricted especially. Even if hydrolysis is hydrolysis by the acid, it may be hydrolysis by alkali, and it can use alkali, such as organic acids, such as inorganic acids, such as a nitric acid and a hydrochloric acid, and a formic acid, and ammonia, for the hydrolysis. It is desirable to use an alkyl halide trimethylammonium system cationic surfactant which was described above as a surface active agent. As other surface active agents, for example, dimethyl DESHIRU benzyl ammoniumchloride, diethyl dodecylbenzyl ammoniumchloride, a trimethyl dodecyl ammonium star's picture, an ARIRUJIBUCHIRU dodecyl ammonium star's picture, diethyl acetonyl dodecyl ammoniumchloride, etc. can also be used.
[0013] As described above, the amount of the above-mentioned raw material used is 8-15 mols about water to one mol of raw material organic silanes, and is 0.5-1.5 mols about an acid or alkali, and it is desirable about a surfactant that it is 0.1-0.4 mols. By choosing suitably the amount used and the heat-treatment conditions of this surfactant, it is possible to produce alternatively porosity SiO2 film which has desired specific inductive capacity.
[0014] As it described above, apply the obtained organic silane liquid by the methods of application, such as the usual spin coat method, on a semi-conductor substrate, and, subsequently heat-treat it using a well-known infrared heating furnace etc., and the organic substance of a water-alcoholic system solvent and a surfactant, and others etc. is made to evaporate, and porosity SiO2 film is produced. The heat-treatment conditions in this case make this solvent, a

surfactant, etc. evaporate, and if it is the conditions which can obtain porous membrane, there will be especially no limit. What is necessary is to process at the temperature of about 200-350 degrees C in air, to be the temperature (for example, 250-500 degrees C) which makes a solvent mainly able to evaporate and can subsequently evaporate the organic substance of a surfactant and others etc. among the vacuum of about 100 to 10 - 5Pa, and just to process preferably, between the time amount by which the structure of the porous membrane obtained is not destroyed, in order to obtain porous membrane with low specific inductive capacity.

[0015] Thus, the verification test was performed [porous membrane / which was obtained] about the hygroscopicity from a film side face as follows. The top face of porosity SiO2 film produced on Si substrate and the side face were covered with the polyimide film. Four of two samples covered with the polyimide film of one sample were cut off, and the cross section of porosity SiO2 film was taken out. The porosity test was performed for the thing with the condition of having covered, and the sample which took out the cross section of porosity SiO2 film on the same conditions, and the existence of the moisture absorption from a porosity SiO2 film side face was seen by comparing the specific inductive capacity after a trial. Consequently, since a difference was not accepted in the specific inductive capacity after the porosity test of a sample [having covered with the polyimide film], and the sample which cut off the side face and took out the cross section of porosity SiO2 film, there is no outlet of a hole in the side face of porosity SiO2 film, and it turns out that orientation of the hole of this porosity SiO2 film is perpendicularly carried out to a substrate.

[0016] Subsequently, on the above-mentioned porous membrane, by the CVD method or the spatter, either SiO2 film of 100nm or less of thickness, the SiNx film or the SiOxNy film is formed, and this porous membrane front face is capped. When the thickness of a cap layer is too thick, the capped insulator layer becomes thick too much, and there is a problem of moving against the flow of the technique of the semi-conductor process which is progressing towards thin-film-izing. Therefore, it is desirable to make it as thin as possible, taking the possible thickness of suppressing hygroscopicity into consideration. Moreover, a cap layer may be carried out further and may be prepared two or more layers.

[0017] Thus, when electrodes, such as an aluminum electrode, are vapor-deposited and specific inductive capacity is measured about hydrophobing porosity SiO2 obtained film, it turns out that the hydrophobing porosity SOG film suitable for the purpose of this invention is obtained. That is, the porosity SOG film without invasion of the moisture to porous membrane which carried out hydrophobing processing is obtained by forming a cap layer in a porosity SiO2 film front face by the above-mentioned approach. Furthermore, even if it carries out the laminating of other film on the porosity SOG film which carried out hydrophobing processing, the interlayer insulation film which does not almost have the rise of the specific inductive capacity of porosity SiO2 film is obtained.

[0018] If organic silanes, such as TEOS or TMOS, are preferably used as described above, it is possible to produce the interlayer insulation film of low specific inductive capacity of 60% or more of voidage, for example. If it reaches, for example to about 80% as voidage becomes high, since the contribution to the specific inductive capacity based on the physical properties of the ingredient which constitutes an insulator layer decreases and the effect of air becomes dominant, the interlayer insulation film of low specific inductive capacity will be obtained. Even if it uses the alkoxide which can be hydrolyzed instead of an organic silane from such a viewpoint, the hydrophobing porous membrane as a low specific-inductive-capacity interlayer insulation film is producible like the case of an organic silane. As such an alkoxide, alcoholates belonging to periodic-table 4A groups, such as Ti (OC3H7)4 and Zr (OC4H9)4, such as Ti and Zr, may be used, for example.

[0019]

[Example] Hereafter, the example of this invention is explained with reference to a drawing.

(Example 1) As a raw material which prepares the reaction mixture for porosity SiO2 film production, SiO2 liquid for porosity SOG film was prepared to one mol of TEOS(s) using the surfactant of 0.7 mols [of nitric acids] H 2O12 mols and 15 mols of ethanol, and the specified quantity. as a surface active agent -- n-hexadecyl trimethylammonium chloride (the product made from Kanto Chemistry, trade name:CTACl) -- one mol of TEOS(s) -- receiving -- 0.1 and 0.15 -- 0. 2 or 0.25 mols added, and coating liquid was prepared. The spin coat of each coating liquid was carried out on condition that 3000 revolutions per minute on the semi-conductor substrate (sample-number A-H). Using the well-known infrared heating furnace, each applied substrate was processed at 200-400 degrees C among air at first, as shown in Table 1, subsequently, baking processing was carried out at 400 degrees C among the ambient atmosphere of 100 to ten to 5 Pa, and porosity SiO2 film was obtained. In this case, time amount which carries out a temperature up from the first processing temperature of 200 degrees C to the processing temperature of 400 degrees C of degree process was made into 60 minutes, and, also in others, it was made into the same programming rate. Although especially this programming rate is not necessarily restricted, there are few film dry areas about the membraneous quality of the obtained film, and it should just be the range where leakage current also serves as a small value. Moreover, that what is necessary is just the range which the film structural failure does not produce, by this example, it held for 30 minutes and the holding time in vacuum firing was calcinated.

[0020] Subsequently, on the front face of porosity SiO2 obtained film (thickness: 0.5 micrometers), by the CVD method or the spatter, SiO2 film, the SiNx film, or the SiOxNy film (thickness: 50nm) was formed, and the front face of this porous membrane was capped.
[0021] Thus, about hydrophobing porosity SiO2 obtained film, after vapor-depositing an aluminum electrode, specific inductive capacity was measured using the specific-inductive-capacity measuring device made from HP (RF IMPEDANCE ANALYZER 4191A). The obtained specific inductive capacity is shown in Table 1.
[0022]
[Table 1]

試料番号	最初の加熱処理(℃)	次工程の加熱処理(℃)	界面活性剤/TEOS(モル比)	比誘電A ($\varepsilon/\varepsilon_0$)	比誘電B ($\varepsilon/\varepsilon_0$)
A	200	400	0.1	3.8	4.0
B	200	400	0.15	3.2	3.4
C	200	400	0.2	2.0	2.3
D	200	400	0.25	1.5	1.7
E	250	400	0.25	1.5	1.8
F	300	400	0.25	2.5	2.7
G	350	400	0.25	3.2	3.4
H	400	400	0.25	4.1	4.4

The inside of Table 1 and specific inductive capacity A are measured about the sample which vapor-deposited the aluminum electrode, without capping the hydrophobic film after forming porous membrane, and after specific inductive capacity B forms porous membrane, they measure it about the sample which vapor-deposited the aluminum electrode to what capped the hydrophobic film.
[0023] When it processed at 200-350 degrees C among air and subsequently processed at 400 degrees C among a vacuum so that clearly from Table 1, the SOG film which has the low specific inductive capacity A of 1.0-4.0 within the limits was obtained, and specific inductive capacity B hardly changed. Furthermore, the obtained hydrophobing porosity SOG film did not almost have the rise of specific inductive capacity, also when the laminating of the film was further carried out on it after formation of this film.
[0024] About the case where the porosity SOG film is produced on a substrate according to the above-mentioned example, and the case where porosity SiO2 film is produced on a substrate with the conventional technique (approach by silanizing inorganic [SOG]), the cross-section photograph (drawing 1) was taken with the scanning electron microscope (SEM), and the membraneous condition of each porous membrane was observed. In the case of the film, from this SEM image, the hole (several nm - dozens of nm) of a big path was observed conventionally, but (drawing 1 (A)) by the SOG film of this invention, it turns out that it is a very small hole and is actually the hole 1nm or less which cannot carry out SEM observation (drawing 1 (B)).
[0025] Moreover, as a surface active agent, also when lauryl trimethylammonium chloride (the Kao Corp. make, trade name:Kohtamin 24P) was used instead of n-hexadecyl trimethylammonium chloride, the same result as the above was obtained.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the production approach of the porosity SOG film, especially the production approach of the hydrophobing porosity SOG film.

[Translation done.]

PRIOR ART

[Description of the Prior Art] While copper (Cu) wiring is introduced in the field of LSI in recent years, the researches and developments about wiring structure, an interlayer insulation film, etc. are done. Since it is difficult to decrease wiring delay effectively only by using Cu wiring, making this oxide film into porosity is proposed from a viewpoint of obtaining the film with still lower specific inductive capacity in a semi-conductor process, using the low specific-inductive-capacity oxide film (SiO2 film) as an interlayer insulation film. For example, forming porosity SiO2 film of low specific inductive capacity by silanizing inorganic [SOG] is proposed using the method of applying the conventional SOG (spin on glass). Moreover, plasma CVD is used, a plasma polymerization is carried out using an organic silane, and forming SiO2 film of low specific inductive capacity is also proposed.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] When the laminating of the film is further carried out on it in semi-conductor processes, such as a CVD process, after formation of SiO2 film by the conventional approach, there is a problem that specific inductive capacity will rise. In the case of porosity SiO2 film formed using inorganic [SOG], in the case of that it is difficult for the path of a hole to become large too much, to form detailed pore, and to make specific inductive capacity a low value, and SiO2 film formed using the organic silane, there are also not enough problems that heat-resistant temperature is low (450 degrees C or less), in respect of membraneous quality.
[0004] Then, this invention persons did patent application as an application for patent No. 101478 [2000 to] as of April 3, Heisei 12 about the production approach of the porosity SOG film that are the interlayer insulation film of low specific inductive capacity, and specific inductive capacity does not change even if it carries out the laminating of the film further on it according to the CVD process after this interlayer insulation film formation etc., in order to cancel the fault of the above-mentioned conventional technique. However, by porosity SiO2 film obtained in this case, since that hole is carrying out orientation perpendicularly to the substrate, invasion of the moisture of the steam from a film front face etc. may become a problem. Moreover, since the inorganic SOG film contains a lot of OH radicals and an unreacted OH radical may remain also after baking, the moisture in an ambient atmosphere sticks to this residual OH radical, and there is also a problem of corroding wiring of aluminum etc.
[0005] This invention is the interlayer insulation film of low specific inductive capacity which prevented invasion of the moisture from a film front face, and suppressed moisture absorption, and even if it carries out the laminating of the film further on it according to the CVD process after this interlayer insulation film formation etc., it makes it a technical problem to offer the production approach of the hydrophobing porosity SOG film that specific inductive capacity does not change, while canceling the fault of the above-mentioned conventional technique.

[Translation done.]

MEANS

[Means for Solving the Problem] this invention persons have developed wholeheartedly so that they may suppress moisture absorption of the obtained film, while they develop wholeheartedly so that they may choose various ingredients and may find out a suitable ingredient and a suitable reaction condition in order to obtain porosity SiO2 film of low specific inductive capacity from a viewpoint that the specific inductive capacity of an interlayer insulation film is so desirable that it is low, with a spin coat method. Consequently, by obtaining porosity SiO2 film, and subsequently capping namely, covering the front face of this porous membrane with the film which consists of a specific ingredient by adding a surfactant to the system of reaction using an organic silane, even if specific inductive capacity is low and forms a cascade screen in the semi-conductor process after film formation, it succeeds in obtaining porosity SiO2 film which does not have change in specific inductive capacity and by which hydrophobing was carried out, and it came to complete this invention.
[0007] Using the organic silane liquid containing an organic silane, water, and alcohol, the production approach of the hydrophobing porosity SOG film of this invention gives this organic silane to acidolysis or alkali hydrolysis, obtains porosity SiO2 film by heat-treating under existence of a surfactant, forms either SiO2 film, the SiNx film or the SiOxNy film in the front face of the porous membrane subsequently obtained by the CVD method or the spatter, and consists of capping this front face. Thereby, while moisture absorption of porous membrane is suppressed, even if it forms a cascade screen in the semi-conductor process of a back process, hydrophobing porosity SiO2 film which does not have change in specific inductive capacity can be obtained.
[0008] An organic silane is an organic oxy-silane of TEOS (tetramethyl orthochromatic silicate) or TMOS (tetramethoxy silane) which can be hydrolyzed. A surfactant A cationic surfactant, especially lauryl trimethylammonium chloride, n-hexadecyl trimethylammonium chloride, an alkyl trimethylammonium star's picture, Cetyl trimethylammonium chloride, a cetyl trimethylammonium star's picture, Stearyl trimethylammonium chloride, alkyldimethyl ethyl ammonium chloride, An alkyldimethyl ethylammonium star's picture, cetyldimethylethyl ammonium bromide, It is desirable that it is the alkyl halide trimethylammonium system cationic surfactant chosen from an octadecyl dimethyl ethylammonium star's picture or methyl dodecylbenzyl trimethylammonium chloride.
[0009] As for the amount of each raw material used, it is desirable to use the acid for 8-15 mols of water, acidolysis, or alkali hydrolysis, 0.5-1.5 mols of alkali, and 0.1-0.4 mols of surfactants to one mol of organic silanes. If the specific inductive capacity of the film obtained as water is less than eight mols does not become small but exceeds 15 mols, the solid-state of SiO2 deposits. A predetermined reaction does not advance with an acid and alkali being less than 0.5 mols, but if it exceeds 1.5 mols, the system of reaction will solidify. The specific inductive capacity of the film obtained as a surfactant is less than 0.1 mols becomes high, and if it exceeds 0.4 mols, membraneous quality will worsen. In addition, it is added in order to adjust the concentration of the whole reaction mixture, and according to the viscosity of reaction mixture, the amount is adjusted and alcohol is added so that it may be easy to apply.
[0010] Moreover, this invention is characterized by providing the following in the production approach of the hydrophobing porosity SOG film. An organic silane Water Alcohol ** which mixes an acid or alkali, carries out the spin coat of the organic silane liquid which added the surfactant further, heat-treats it on a semi-conductor substrate, obtains porosity SiO2 film as an interlayer insulation film by making this water, alcohol, and a surfactant evaporate, forms either SiO2 film, the SiNx film or the SiOxNy film in the front face of the porous membrane subsequently obtained by the CVD method or the spatter, and caps this front face
[0011]
[Embodiment of the Invention] The production approach of hydrophobing porosity SiO2 film of this invention As described above, the organic silane liquid containing an organic silane, water, and alcohol is used. Apply what added the surfactant in the liquid obtained by ****** which gives this to acidolysis or alkali hydrolysis on a semi-conductor substrate, and it is heated under existence of a surfactant. Porosity SiO2 film is obtained by removing the matter, evaporating water, alcohol, and a surfactant, when other organic substances etc. are contained in the system of reaction

and. Subsequently By the CVD method or the spatter, the hydrophobic film is formed in the front face of the obtained porous membrane, and this front face is capped. It becomes possible by many opening parts' (voidage's: about 60%'s or more) arising in the film, and becoming porosity in this way, and capping this porous membrane by the specific film to suppress invasion of moisture as a surfactant evaporates.

[0012] If it is the organic oxy-silane which was described above and which can be decomposed as a raw material silane, it will be used without being restricted especially. As alcohol, if it is alcoholic system solvents, such as ethyl alcohol and isopropyl alcohol, it will be used, without being restricted especially. Even if hydrolysis is hydrolysis by the acid, it may be hydrolysis by alkali, and it can use alkali, such as organic acids, such as inorganic acids, such as a nitric acid and a hydrochloric acid, and a formic acid, and ammonia, for the hydrolysis. It is desirable to use an alkyl halide trimethylammonium system cationic surfactant which was described above as a surface active agent. As other surface active agents, for example, dimethyl DESHIRU benzyl ammoniumchloride, diethyl dodecylbenzyl ammoniumchloride, a trimethyl dodecyl ammonium star's picture, an ARIRUJIBUCHIRU dodecyl ammonium star's picture, diethyl acetonyl dodecyl ammoniumchloride, etc. can also be used.

[0013] As described above, the amount of the above-mentioned raw material used is 8-15 mols about water to one mol of raw material organic silanes, and is 0.5-1.5 mols about an acid or alkali, and it is desirable about a surfactant that it is 0.1-0.4 mols. By choosing suitably the amount used and the heat-treatment conditions of this surfactant, it is possible to produce alternatively porosity SiO2 film which has desired specific inductive capacity.

[0014] As it described above, apply the obtained organic silane liquid by the methods of application, such as the usual spin coat method, on a semi-conductor substrate, and, subsequently heat-treat it using a well-known infrared heating furnace etc., and the organic substance of a water-alcoholic system solvent and a surfactant, and others etc. is made to evaporate, and porosity SiO2 film is produced. The heat-treatment conditions in this case make this solvent, a surfactant, etc. evaporate, and if it is the conditions which can obtain porous membrane, there will be especially no limit. What is necessary is to process at the temperature of about 200-350 degrees C in air, to be the temperature (for example, 250-500 degrees C) which makes a solvent mainly able to evaporate and can subsequently evaporate the organic substance of a surfactant and others etc. among the vacuum of about 100 to 10 - 5Pa, and just to process preferably, between the time amount by which the structure of the porous membrane obtained is not destroyed, in order to obtain porous membrane with low specific inductive capacity.

[0015] Thus, the verification test was performed [porous membrane / which was obtained] about the hygroscopicity from a film side face as follows. The top face of porosity SiO2 film produced on Si substrate and the side face were covered with the polyimide film. Four of two samples covered with the polyimide film of one sample were cut off, and the cross section of porosity SiO2 film was taken out. The porosity test was performed for the thing with the condition of having covered, and the sample which took out the cross section of porosity SiO2 film on the same conditions, and the existence of the moisture absorption from a porosity SiO2 film side face was seen by comparing the specific inductive capacity after a trial. Consequently, since a difference was not accepted in the specific inductive capacity after the porosity test of a sample [having covered with the polyimide film], and the sample which cut off the side face and took out the cross section of porosity SiO2 film, there is no outlet of a hole in the side face of porosity SiO2 film, and it turns out that orientation of the hole of this porosity SiO2 film is perpendicularly carried out to a substrate.

[0016] Subsequently, on the above-mentioned porous membrane, by the CVD method or the spatter, either SiO2 film of 100nm or less of thickness, the SiNx film or the SiOxNy film is formed, and this porous membrane front face is capped. When the thickness of a cap layer is too thick, the capped insulator layer becomes thick too much, and there is a problem of moving against the flow of the technique of the semi-conductor process which is progressing towards thin-film-izing. Therefore, it is desirable to make it as thin as possible, taking the possible thickness of suppressing hygroscopicity into consideration. Moreover, a cap layer may be carried out further and may be prepared two or more layers.

[0017] Thus, when electrodes, such as an aluminum electrode, are vapor-deposited and specific inductive capacity is measured about hydrophobing porosity SiO2 obtained film, it turns out that the hydrophobing porosity SOG film suitable for the purpose of this invention is obtained. That is, the porosity SOG film without invasion of the moisture to porous membrane which carried out hydrophobing processing is obtained by forming a cap layer in a porosity SiO2 film front face by the above-mentioned approach. Furthermore, even if it carries out the laminating of other film on the porosity SOG film which carried out hydrophobing processing, the interlayer insulation film which does not almost have the rise of the specific inductive capacity of porosity SiO2 film is obtained.

[0018] If organic silanes, such as TEOS or TMOS, are preferably used as described above, it is possible to produce the interlayer insulation film of low specific inductive capacity of 60% or more of voidage, for example. If it reaches, for example to about 80% as voidage becomes high, since the contribution to the specific inductive capacity based on the physical properties of the ingredient which constitutes an insulator layer decreases and the effect of air becomes dominant, the interlayer insulation film of low specific inductive capacity will be obtained. Even if it uses the alkoxide

which can be hydrolyzed instead of an organic silane from such a viewpoint, the hydrophobing porous membrane as a low specific-inductive-capacity interlayer insulation film is producible like the case of an organic silane. As such an alkoxide, alcoholates belonging to periodic-table 4A groups, such as Ti $(OC3H7)4$ and Zr $(OC4H9)4$, such as Ti and Zr, may be used, for example.

[Translation done.]

EXAMPLE

[Example] Hereafter, the example of this invention is explained with reference to a drawing.
(Example 1) As a raw material which prepares the reaction mixture for porosity SiO2 film production, SiO2 liquid for porosity SOG film was prepared to one mol of TEOS(s) using the surfactant of 0.7 mols [of nitric acids] H 2O12 mols and 15 mols of ethanol, and the specified quantity. as a surface active agent -- n-hexadecyl trimethylammonium chloride (the product made from Kanto Chemistry, trade name:CTACl) -- one mol of TEOS(s) -- receiving -- 0.1 and 0.15 -- 0. 2 or 0.25 mols added, and coating liquid was prepared. The spin coat of each coating liquid was carried out on condition that 3000 revolutions per minute on the semi-conductor substrate (sample-number A-H). Using the well-known infrared heating furnace, each applied substrate was processed at 200-400 degrees C among air at first, as shown in Table 1, subsequently, baking processing was carried out at 400 degrees C among the ambient atmosphere of 100 to ten to 5 Pa, and porosity SiO2 film was obtained. In this case, time amount which carries out a temperature up from the first processing temperature of 200 degrees C to the processing temperature of 400 degrees C of degree process was made into 60 minutes, and, also in others, it was made into the same programming rate. Although especially this programming rate is not necessarily restricted, there are few film dry areas about the membraneous quality of the obtained film, and it should just be the range where leakage current also serves as a small value. Moreover, that what is necessary is just the range which the film structural failure does not produce, by this example, it held for 30 minutes and the holding time in vacuum firing was calcinated.
[0020] Subsequently, on the front face of porosity SiO2 obtained film (thickness: 0.5 micrometers), by the CVD method or the spatter, SiO2 film, the SiNx film, or the SiOxNy film (thickness: 50nm) was formed, and the front face of this porous membrane was capped.
[0021] Thus, about hydrophobing porosity SiO2 obtained film, after vapor-depositing an aluminum electrode, specific inductive capacity was measured using the specific-inductive-capacity measuring device made from HP (RF IMPEDANCE ANALYZER 4191A). The obtained specific inductive capacity is shown in Table 1.
[0022]
[Table 1]

試料番号	最初の加熱処理(℃)	次工程の加熱処理(℃)	界面活性剤/TEOS(モル比)	比誘電A (ε/ε₀)	比誘電B (ε/ε₀)
A	200	400	0. 1	3. 8	4. 0
B	200	400	0. 15	3. 2	3. 4
C	200	400	0. 2	2. 0	2. 3
D	200	400	0. 25	1. 5	1. 7
E	250	400	0. 25	1. 5	1. 8
F	300	400	0. 25	2. 5	2. 7
G	350	400	0. 25	3. 2	3. 4
H	400	400	0. 25	4. 1	4. 4

The inside of Table 1 and specific inductive capacity A are measured about the sample which vapor-deposited the aluminum electrode, without capping the hydrophobic film after forming porous membrane, and after specific inductive capacity B forms porous membrane, they measure it about the sample which vapor-deposited the aluminum electrode to what capped the hydrophobic film.
[0023] When it processed at 200-350 degrees C among air and subsequently processed at 400 degrees C among a vacuum so that clearly from Table 1, the SOG film which has the low specific inductive capacity A of 1.0-4.0 within the limits was obtained, and specific inductive capacity B hardly changed. Furthermore, the obtained hydrophobing

porosity SOG film did not almost have the rise of specific inductive capacity, also when the laminating of the film was further carried out on it after formation of this film.

[0024] About the case where the porosity SOG film is produced on a substrate according to the above-mentioned example, and the case where porosity SiO2 film is produced on a substrate with the conventional technique (approach by silanizing inorganic [SOG]), the cross-section photograph (drawing 1) was taken with the scanning electron microscope (SEM), and the membraneous condition of each porous membrane was observed. In the case of the film, from this SEM image, the hole (several nm - dozens of nm) of a big path was observed conventionally, but (drawing 1 (A)) by the SOG film of this invention, it turns out that it is a very small hole and is actually the hole 1nm or less which cannot carry out SEM observation (drawing 1 (B)).

[0025] Moreover, as a surface active agent, also when lauryl trimethylammonium chloride (the Kao Corp. make, trade name:Kohtamin 24P) was used instead of n-hexadecyl trimethylammonium chloride, the same result as the above was obtained.

[Translation done.]

DESCRIPTION OF DRAWINGS

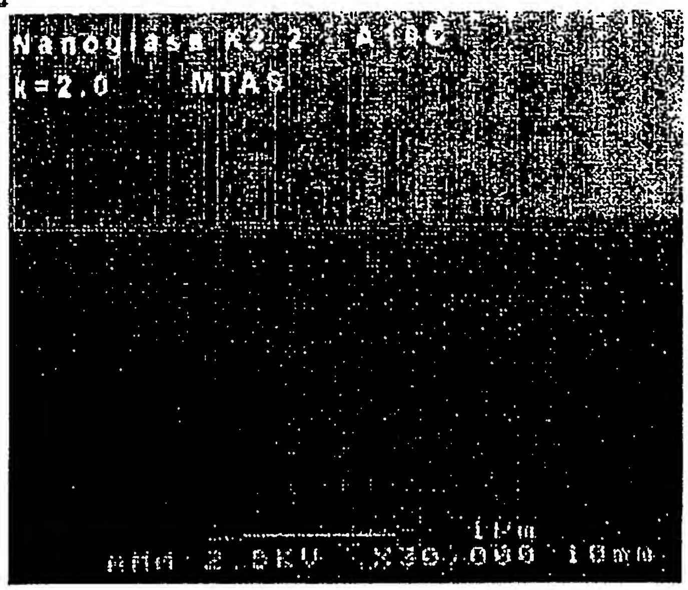
[Brief Description of the Drawings]
[Drawing 1] (A) The scanning electron microscope (SEM) photograph about the cross section of the porous membrane obtained according to the conventional technique.
(B) The scanning electron microscope (SEM) photograph about the cross section of the porous membrane obtained according to this invention.

[Translation done.]

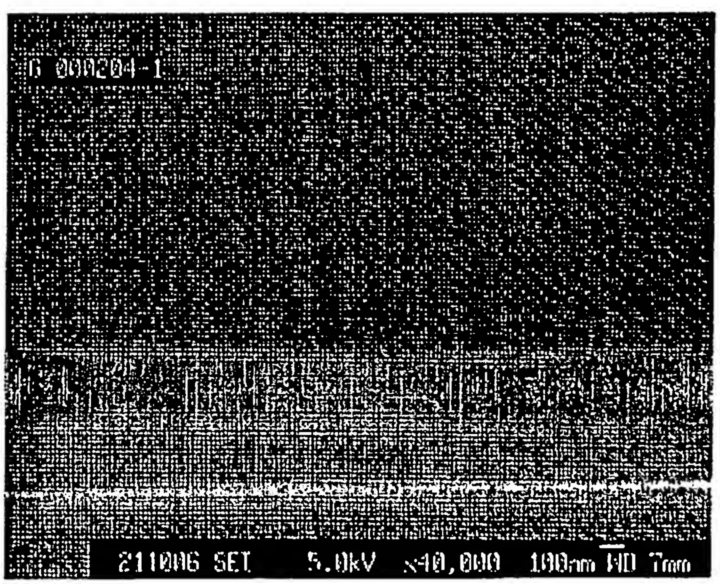
DRAWINGS

[Drawing 1]

(A)



(B)



[Translation done.]

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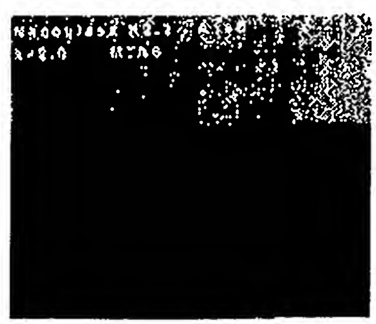
(54)【発明の名称】 疎水化多孔質SOG膜の作製方法

(57)【要約】
【課題】 膜表面からの水分の侵入を防ぎ、吸湿を抑えた、低比誘電率の層間絶縁膜であって、この膜形成後のCVDプロセスなどによりその上にさらに膜を積層させても、比誘電率が変化しない疎水化多孔質SOG膜の作製方法の提供。
【解決手段】 有機シランと、水と、アルコールとを含む有機シラン液を用い、該有機シランを酸加水分解またはアルカリ加水分解に付し、界面活性剤の存在下で加熱処理することにより多孔質SiO_2膜を得、次いで、CVD法またはスパッタ法により、得られた多孔質膜の表面にSiO_2膜、SiN_x膜またはSiO_xN_y膜のいずれかを形成し、該表面をキャップする。

(A)



(B)

【特許請求の範囲】

【請求項１】　有機シランと、水と、アルコールとを含む有機シラン液を用い、該有機シランを酸加水分解またはアルカリ加水分解に付し、界面活性剤の存在下で加熱処理することにより多孔質SiO_2膜を得、次いで、ＣＶＤ法またはスパッタ法により、得られた多孔質膜の表面にSiO_2膜、SiN_x膜またはSiO_xN_y膜のいずれかを形成し、該表面をキャップすることを特徴とする疎水化多孔質ＳＯＧ膜の作製方法。

【請求項２】　前記有機シランが加水分解可能な有機オキシシランであり、界面活性剤が陽イオン性界面活性剤であることを特徴とする請求項１記載の疎水化多孔質ＳＯＧ膜の作製方法。

【請求項３】　前記有機シランがＴＥＯＳまたはＴＭＯＳであり、界面活性剤がラウリルトリメチルアンモニウムクロライド、ｎ－ヘキサデシルトリメチルアンモニウムクロライド、アルキルトリメチルアンモニウムブロマイド、セチルトリメチルアンモニウムクロライド、セチルトリメチルアンモニウムブロマイド、ステアリルトリメチルアンモニウムクロライド、アルキルジメチルエチルアンモニウムクロライド、アルキルジメチルエチルアンモニウムブロマイド、セチルジメチルエチルアンモニウムブロマイド、オクタデシルジメチルエチルアンモニウムブロマイド、またはメチルドデシルベンジルトリメチルアンモニウムクロライドなどから選ばれたハロゲン化アルキルトリメチルアンモニウム系陽イオン性界面活性剤であることを特徴とする請求項１または２記載の疎水化多孔質ＳＯＧ膜の作製方法。

【請求項４】　前記有機シラン１モルに対して、水８～１５モル、酸加水分解またはアルカリ加水分解のための酸やアルカリ０．５～１．５モル、界面活性剤０．１～０．４モルを用いることを特徴とする請求項１～３のいずれかに記載の疎水化多孔質ＳＯＧ膜の作製方法。

【請求項５】　有機シランと、水と、アルコールと、酸またはアルカリとを混合し、さらに界面活性剤を添加した有機シラン液を半導体基板上にスピンコートし、加熱処理して、該水、アルコール、界面活性剤を蒸発せしめることにより多孔質SiO_2膜を得、次いで、ＣＶＤ法またはスパッタ法により、得られた多孔質膜の表面にSiO_2膜、SiN_x膜またはSiO_xN_y膜のいずれかを形成し、該表面をキャップすることを特徴とする疎水化多孔質ＳＯＧ膜の作製方法。

【発明の詳細な説明】

【０００１】

ついての研究開発が行われている。Ｃｕ配線を用いるだけでは配線遅延を効果的に減少することが困難であるため、半導体プロセスにおいて層間絶縁膜として低比誘電率酸化物膜（SiO_2膜）を用い、さらに、比誘電率の低い膜を得るという観点から、この酸化物膜を多孔質にすることが提案されている。例えば、従来のＳＯＧ(spin on glass)の塗布法を利用して、無機ＳＯＧのシリル化により低比誘電率の多孔質SiO_2膜を形成することが提案されている。また、プラズマＣＶＤを利用し、有機シランを用いてプラズマ重合し、低比誘電率のSiO_2膜を形成することも提案されている。

【０００３】

【発明が解決しようとする課題】従来の方法によるSiO_2膜の形成後に、ＣＶＤプロセスなどの半導体プロセスにおいてその上にさらに膜を積層させると、比誘電率が上昇してしまうという問題がある。無機ＳＯＧを用いて形成した多孔質SiO_2膜の場合は、空孔の径が大きくなり過ぎてしまい、微細な細孔を形成して比誘電率を低い値にすることが困難であること、また、有機シランを用いて形成したSiO_2膜の場合は、膜質の点で十分でなく、また、耐熱温度が低い（４５０℃以下）という問題もある。

【０００４】そこで、本発明者らは、上記従来技術の欠点を解消するために、低比誘電率の層間絶縁膜であって、この層間絶縁膜形成後のＣＶＤプロセスなどによりその上にさらに膜を積層させても、比誘電率が変化しない多孔質ＳＯＧ膜の作製方法について平成１２年４月３日付けで特願２０００－１０１４７８号として特許出願した。しかしながら、この場合、得られた多孔質SiO_2膜では、その空孔が基板に対して垂直に配向しているので、膜表面からの水蒸気などの水分の侵入が問題になることがある。また、無機ＳＯＧ膜は多量のＯＨ基を含んでいるため、焼成後でも未反応のＯＨ基が残留することがあるので、この残留ＯＨ基に雰囲気中の水分が吸着し、Ａｌなどの配線を腐食するという問題もある。

【０００５】本発明は、上記従来技術の欠点を解消すると共に、膜表面からの水分の侵入を防ぎ、吸湿を抑えた、低比誘電率の層間絶縁膜であって、この層間絶縁膜形成後のＣＶＤプロセスなどによりその上にさらに膜を積層させても、比誘電率が変化しない疎水化多孔質ＳＯＧ膜の作製方法を提供することを課題とする。

【０００６】

【課題を解決するための手段】本発明者らは、層間絶縁膜の比誘電率は低い程好ましいという観点から、スピン

特定の材料からなる膜でキャップする、すなわち被覆することにより、比誘電率が低く、膜形成後の半導体プロセスにおいて積層膜を形成しても比誘電率に変化のない疎水化された多孔質SiO_2膜を得ることに成功し、本発明を完成させるに至った。

【０００７】本発明の疎水化多孔質ＳＯＧ膜の作製方法は、有機シランと、水と、アルコールとを含む有機シラン液を用い、該有機シランを酸加水分解またはアルカリ加水分解に付し、界面活性剤の存在下で加熱処理することにより多孔質SiO_2膜を得、次いで、ＣＶＤ法またはスパッタ法により、得られた多孔質膜の表面にSiO_2膜、SiN_x膜またはSiO_xN_y膜のいずれかを形成し、該表面をキャップすることからなる。これにより、多孔質膜の吸湿が抑えられると共に、後工程の半導体プロセスにおいて積層膜を形成しても比誘電率に変化のない疎水化多孔質SiO_2膜を得ることができる。

【０００８】有機シランは、ＴＥＯＳ（テトラメチルオルソシリケート）またはＴＭＯＳ（テトラメトキシシラン）などのような加水分解可能な有機オキシシランであり、界面活性剤は、陽イオン性界面活性剤、特にラウリルトリメチルアンモニウムクロライド、ｎ－ヘキサデシルトリメチルアンモニウムクロライド、アルキルトリメチルアンモニウムブロマイド、セチルトリメチルアンモニウムクロライド、セチルトリメチルアンモニウムブロマイド、ステアリルトリメチルアンモニウムクロライド、アルキルジメチルエチルアンモニウムクロライド、アルキルジメチルエチルアンモニウムブロマイド、セチルジメチルエチルアンモニウムブロマイド、オクタデシルジメチルエチルアンモニウムブロマイド、またはメチルドデシルベンジルトリメチルアンモニウムクロライドなどから選ばれたハロゲン化アルキルトリメチルアンモニウム系陽イオン性界面活性剤であることが好ましい。

【０００９】各原料の使用量は、有機シラン１モルに対して、水８～１５モル、酸加水分解またはアルカリ加水分解のための酸やアルカリ０．５～１．５モル、界面活性剤０．１～０．４モルを用いることが好ましい。水が８モル未満であると得られる膜の比誘電率が小さくならず、１５モルを超えるとSiO_2の固体が析出する。酸やアルカリが０．５モル未満であると所定の反応が進行せず、１．５モルを超えると反応系が固まってしまう。界面活性剤が０．１モル未満であると得られる膜の比誘電率は高くなり、０．４モルを超えると膜質が悪くなる。なお、アルコールは、反応液全体の濃度を調整するために添加されるものであり、反応液の粘性に応じて、

とにより層間絶縁膜としての多孔質SiO_2膜を得、次いで、ＣＶＤ法またはスパッタ法により、得られた多孔質膜の表面にSiO_2膜、SiN_x膜またはSiO_xN_y膜のいずれかを形成し、該表面をキャップすることからなる。

【００１１】

【発明の実施の形態】本発明の疎水化多孔質SiO_2膜の作製方法は、上記したように、有機シランと、水と、アルコールとを含む有機シラン液を用い、これを酸加水分解またはアルカリ加水分解に付することにより得た液に界面活性剤を添加したものを、半導体基板上に塗布し、界面活性剤の存在下で加熱して、水、アルコール、界面活性剤を蒸発させながら、また、反応系にその他の有機物質などが含まれている場合にはその物質を取り除くことにより、多孔質SiO_2膜を得、次いで、ＣＶＤ法またはスパッタ法により、得られた多孔質膜の表面に疎水性の膜を形成し、該表面をキャップするものである。界面活性剤が蒸発するにつれて、膜内に多数の空隙部分（空隙率：約６０％以上）が生じ、かくして多孔質となり、また、この多孔質膜を特定の膜でキャップすることにより水分の侵入を抑えることが可能となる。

【００１２】原料シランとしては、上記したような分解可能な有機オキシシランであれば、特に制限されることなく用いられる。アルコールとしては、エチルアルコール、イソプロピルアルコールなどのアルコール系溶媒であれば、特に制限されることなく用いられる。加水分解は、酸による加水分解であってもアルカリによる加水分解であってもよく、その加水分解のために、硝酸や塩酸などの無機酸、ギ酸などの有機酸、アンモニアなどのアルカリを用いることができる。界面活性剤としては、上記したようなハロゲン化アルキルトリメチルアンモニウム系陽イオン性界面活性剤を用いることが好ましい。その他の界面活性剤として、例えばジメチルデシルベンジルアンモニウムクロライド、ジエチルドデシルベンジルアンモニウムクロライド、トリメチルドデシルアンモニウムブロマイド、アリルジブチルドデシルアンモニウムブロマイド、ジエチルアセトニルドデシルアンモニウムクロライドなどを用いることもできる。

【００１３】上記原料の使用量は、上記したように、原料有機シラン１モルに対して、水については８～１５モルであり、酸やアルカリについては０．５～１．５モルであり、界面活性剤については０．１～０．４モルであることが好ましい。この界面活性剤の使用量と加熱処理条件とを適宜選択することにより、所望の比誘電率を有

その他の有機物質などを蒸発せしめ、多孔質SiO_2膜を作製する。この場合の加熱処理条件は、該溶媒および界面活性剤などを蒸発せしめ、多孔質膜を得ることができる条件であれば、特に制限はない。比誘電率の低い多孔質膜を得るためには、好ましくは、空気中で２００〜３５０℃程度の温度で処理して主として溶媒を蒸発せしめ、次いで、例えば１００〜10^{-3}Ｐａ程度の真空中、界面活性剤その他の有機物質などを蒸発させることのできる温度（例えば、２５０〜５００℃）で、得られる多孔質膜の構造が破壊されない時間の間処理すればよい。

【００１５】このようにして得られた多孔質膜について、次のように膜側面からの吸湿性について確認試験を行った。Ｓｉ基板上に作製した多孔質SiO_2膜の上面、側面をポリイミド膜により被覆した。ポリイミド膜で被覆した２つのサンプルのうち一方のサンプルの４辺を切り落として多孔質SiO_2膜の断面を出した。被覆した状態のままのものと、多孔質SiO_2膜の断面を出したサンプルとを同一条件で吸湿試験を行い、試験後の比誘電率を比較することで多孔質SiO_2膜側面からの吸湿の有無をみた。その結果、ポリイミド膜で被覆したままのサンプルと、側面を切り落として多孔質SiO_2膜の断面を出したサンプルの吸湿試験後の比誘電率に差が認められなかったことから、多孔質SiO_2膜の側面には空孔の出口はなく、この多孔質SiO_2膜の空孔は、基板に対して垂直に配向していることが分かる。

【００１６】次いで、上記多孔質膜上に、ＣＶＤ法またはスパッタ法により、例えば膜厚１００ｎｍ以下のSiO_2膜、SiN_x膜またはSiO_xN_y膜のいずれかを形成し、該多孔質膜表面をキャップする。キャップ層の膜厚が厚すぎると、キャップされた絶縁膜が厚くなりすぎてしまい、薄膜化の方向に進んでいる半導体プロセスの技術の流れに逆行するという問題がある。従って、吸湿性を抑えることの可能な膜厚を考慮しながらできるだけ薄くすることが好ましい。また、キャップ層は一層でもよいし、複数層設けてもよい。

【００１７】このようにして得られた疎水化多孔質SiO_2膜について、アルミ電極などの電極を蒸着して比誘電率を測定すると、本発明の目的に合った疎水化多孔質ＳＯＧ膜が得られていることがわかる。すなわち、上記の方法により多孔質SiO_2膜表面にキャップ層を形成することで、多孔質膜への水分の侵入のない、疎水化処理した多孔質ＳＯＧ膜が得られる。さらに、疎水化処理した多孔質ＳＯＧ膜上に他の膜を積層させても、多孔質SiO_2膜の比誘電率の上昇がほとんどない層間絶縁膜

６０％以上の低比誘電率の層間絶縁膜を作製することが可能である。空隙率が高くなるに従って、例えば８０％程に達すると、絶縁膜を構成する材料の物性に基づく比誘電率に対する寄与は少なくなり、空気の影響が支配的になるため、低比誘電率の層間絶縁膜が得られる。このような観点から、有機シランの代わりに加水分解可能なアルコキシドを用いても、有機シランの場合と同様に、低比誘電率層間絶縁膜としての疎水化多孔質膜を作製することができる。このようなアルコキシドとしては、例えば、$Ti(OC_3H_7)_4$、$Zr(OC_4H_9)_4$などの周期表４Ａ族に属するＴｉ、Ｚｒなどのアルコラートが用いられ得る。

【００１９】

【実施例】以下、本発明の実施例を図面を参照して説明する。

（実施例１）多孔質SiO_2膜作製のための反応液を調製する原料として、ＴＥＯＳ１モルに対して、硝酸０．７モル、H_2O１２モル、エタノール１５モル、所定量の界面活性剤を用い、多孔質ＳＯＧ膜用のSiO_2液を調製した。界面活性剤として、ｎ−ヘキサデシルトリメチルアンモニウムクロライド（関東化学（株）製、商品名：ＣＴＡＣｌ）を、ＴＥＯＳ１モルに対して０．１、０．１５、０．２、０．２５モル添加して、塗布液を調製した。半導体基板（試料番号Ａ〜Ｈ）上に各塗布液を３０００回転／分の条件でスピンコートした。公知の赤外線加熱炉を用いて、塗布された各基板を表１に示すように、最初、空気中２００〜４００℃で処理し、次いで、１００〜10^{-3}Ｐａの雰囲気中４００℃で焼成処理し、多孔質SiO_2膜を得た。この場合、最初の処理温度２００℃から次工程の処理温度４００℃へと昇温する時間を６０分とし、その他の場合も同じ昇温速度とした。この昇温速度は特に制限される訳ではないが、得られた膜の膜質について、膜荒れが少なく、リーク電流も小さな値となるような範囲であればよい。また、真空焼成中の保持時間は膜構造の破壊が生じない範囲であればよく、本実施例では３０分間保持して焼成した。

【００２０】次いで、得られた多孔質SiO_2膜（膜厚：０．５μｍ）の表面に、ＣＶＤ法またはスパッタ法により、SiO_2膜、SiN_x膜またはSiO_xN_y膜（膜厚：５０ｎｍ）を形成し、該多孔質膜の表面をキャップした。

【００２１】このようにして得られた疎水化多孔質SiO_2膜について、アルミ電極を蒸着した後、HP社製比誘電率測定装置(RF IMPEDANCE ANALYZER 4191A)を用いて

試料番号	最初の加熱処理(℃)	次工程の加熱処理(℃)	界面活性剤/TEOS(モル比)	比誘電率A (ε/ε₀)	比誘電率B (ε/ε₀)
A	２００	４００	０．１	３．８	４．０
B	２００	４００	０．１５	３．２	３．４
C	２００	４００	０．２	２．０	２．３
D	２００	４００	０．２５	１．６	１．７
E	２５０	４００	０．２５	１．５	１．８
F	３００	４００	０．２５	２．５	２．７
G	３５０	４００	０．２５	３．２	３．４
H	４００	４００	０．２５	４．１	４．４

表１中、比誘電率Ａは、多孔質膜を形成した後、疎水性膜をキャップすることなくアルミ電極を蒸着した試料について測定したものであり、また、比誘電率Ｂは、多孔質膜を形成した後、疎水性膜をキャップしたものにアルミ電極を蒸着した試料について測定したものである。

【００２３】表１から明らかなように、空気中２００～３５０℃で処理し、次いで真空中４００℃で処理した場合、１．０～４．０の範囲内の低い比誘電率Ａを有するＳＯＧ膜が得られ、また、比誘電率Ｂもほとんど変化しなかった。さらに、得られた疎水化多孔質ＳＯＧ膜は、該膜の形成後にその上にさらに膜を積層させた場合も、比誘電率の上昇がほとんどなかった。

【００２４】上記実施例に従って基板上に多孔質ＳＯＧ膜を作製した場合と、従来技術（無機ＳＯＧのシリル化による方法）により基板上に多孔質ＳｉO_2膜を作製した場合とについて、走査型電子顕微鏡（ＳＥＭ）によりその断面写真（図１）をとり、各多孔質膜の膜質状態を観測した。このＳＥＭ像から、従来膜の場合、大きな径の空孔（数ｎｍ～数十ｎｍ）が観測されたが（図１（Ａ））、本発明のＳＯＧ膜では極めて小さな空孔であり、実際、ＳＥＭ観測できない１ｎｍ以下の空孔であることがわかる(図１(Ｂ))。

【００２５】また、界面活性剤として、ｎ－ヘキサデシルトリメチルアンモニウムクロライドの代わりにラウリルトリメチルアンモニウムクロライド（花王(株)製、商品名：コータミン２４Ｐ）を使用した場合も、上記と同様な結果が得られた。

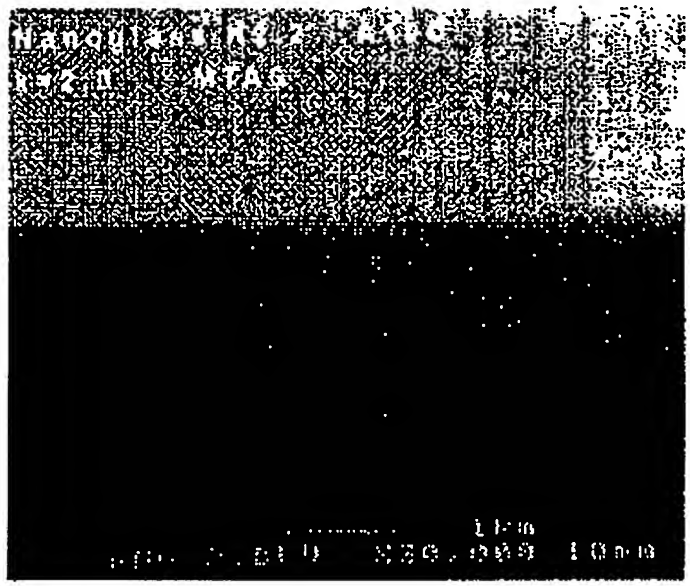
【図面の簡単な説明】

【図１】（Ａ）　従来技術に従って得られた多孔質膜の断面についての走査型電子顕微鏡（ＳＥＭ）写真。

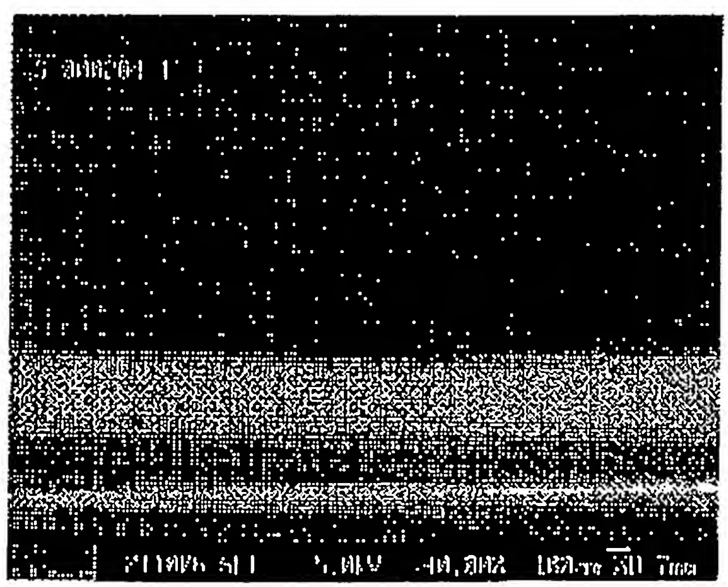
（Ｂ）　本発明に従って得られた多孔質膜の断面についての走査型電子顕微鏡(ＳＥＭ)写真。

【図1】

(A)



(B)



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